PAT-NO: JP411120821A

DOCUMENT-IDENTIFIER: JP 11120821 A

TITLE: **THICK-FILM** SILVER TERMINATED COMPOSITION

PUBN-DATE: April 30, 1999

INVENTOR-INFORMATION:

NAME	COUNTRY
OSBORNE, JAMES	N/A
SIUTA, VINCENT PAUL	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
E I DU PONT DE NEMOURS & CO	N/A

APPL-NO: JP10214655

APPL-DATE: July 29, 1998

PRIORITY-DATA: 97901975 (July 29, 1997)

INT-CL (IPC): H01B001/22, H01C007/00

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a terminated composition for reducing the length effect of a resistor terminated by silver at a low cost.

SOLUTION: This **thick-film** silver terminated composition contains (a) 60-80 wt.% of **silver powder,** (b) 0.1-15 wt.% of glass binder having a softening point of 400-650°C and absolute viscosity less than 106 poise at a burning temperature, (c) a 0.1-5 wt.% of negative TCR driver, with (a), (b), (c) dispersed in an **organic vehicle**. The negative TCR driver is a composition which can be substituted with a hydride of a metal of a group four or a group five in the periodic table. The negative TCR driver can also be

substituted
with a selected metal powder or the metal powder which can be combined with a
hydride or a driver.

COPYRIGHT: (C)1999,JPO

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] It is :a. on the basis of all constituents. 60 - 80 % of the weight of silver dust objects;
b. Set to 400-650-degree C softening temperature and burning temperature, and it is 106. 0.1 - 15 % of the weight of particles of a glass binder which have the absolute viscosity of under a poise;
c. The thick-film silver termination constituent characterized by distributing a, b, and c in an organic vehicle here including 0.1 - 5 % of the weight of negative TCR drivers, and;.
[Claim 2] It is :a. on the basis of all constituents. 60 - 80 % of the weight of silver dust objects;
b. Set to 400-650-degree C softening temperature and burning temperature, and it is 106. 0.1 - 15 % of the weight of particles of a glass binder which have the absolute viscosity of under a poise;
c. The thick-film silver termination constituent characterized by distributing a, b, and c in an organic vehicle here including 0.1 - 5 % of the weight of hydrides of the metal of the 4th group of a periodic table, and the 5th group, and;.
[Claim 3] It considers as all constituent criteria and is :a. 60 - 80 % of the weight of silver dust objects;
b. Set to 400-650-degree C softening temperature and burning temperature, and it is 106. 0.1 - 15 % of the weight of particles of a glass binder which have the absolute viscosity of under a poise;
c. The thick-film silver termination constituent characterized by distributing a, b, and c in an organic vehicle here including 0.1 - 5 % of the weight of metal fine particles and; which are chosen from the group which consists of Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb.
[Claim 4] The constituent according to claim 1 characterized by choosing said negative TCR driver from the group of the oxide of Ta, Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb.
[Claim 5] The hydride of said metal is TiH2, ZrH2, HfH2, CbH2, and ThH4. And constituent according to claim 2 characterized by being chosen from the group which consists of TaH.
[Claim 6] The constituent according to claim 1 characterized by having the metal fine particles chosen from the group which furthermore consists of Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb.
[Claim 7] The constituent according to claim 2 characterized by having the metal fine

particles chosen from the group which furthermore consists of Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb.

[Claim 8] The constituent according to claim 1 characterized by said glass binder being boric-acid bismuth lead glass.

[Claim 9] The constituent according to claim 2 characterized by said glass binder being boric-acid bismuth lead glass.

[Claim 10] The constituent according to claim 3 characterized by said glass binder being boric-acid bismuth lead glass.

[Claim 11] The constituent according to claim 1 characterized by having said 0.1 - 10% of the weight of glass binder.

[Claim 12] The constituent according to claim 2 characterized by having said 0.1 - 10% of the weight of glass binder.

[Claim 13] The constituent according to claim 3 characterized by having said 0.1 - 10% of the weight of glass binder.

[Claim 14] The constituent according to claim 1 characterized by being within the limits said whose burning temperature is 800-900 degrees C.

[Claim 15] The constituent according to claim 2 characterized by being within the limits said whose burning temperature is 800-900 degrees C.

[Claim 16] The constituent according to claim 3 characterized by being within the limits said whose burning temperature is 800-900 degrees C.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is the thick-film silver termination (termination) containing the negative driver or the metal hydride of a temperature coefficient of resistance (TCR). It is related with a constituent.
[0002]
[Description of the Prior Art] Since it is becoming a trend on industry to create a cheaper smaller and electronic instrument, it has been necessary to reduce the size and the price of components like the thick-film chip resistor object in such an electronic instrument, and a hybrid resistor.
[0003] For this, the die length of low cost is termination (terminate) about a resistor with a small configuration of less than 2mm. The termination with abundant silver to carry out realizes. It TCR by which the resistor was measured is not only the function of resistor ink, but is dependent on a termination ingredient like a conductor runner (runner). TCR is (temperature coefficient of resistivity) - (coefficient of thermal expansion) as used here. The combination of typical resistor/conductor was shown in drawing 1 . The both ends of a resistor have terminated this combination by the conductor runner 12 including the substrate 20 which has the resistor 10 printed on that substrate. The near interface field 14 will also be shown in a terminal to the both ends of a resistor soon. The interface field 14 is a field of the resistor which is easy to be influenced of diffusion by the silver from a conductor.
[0004] In preparation of this combination, printing and baking of a resistor ingredient are preceded, and a conductor is printed and calcinated. A conductor may be calcinated by the approach of common use, for example, is performed in the cycle of 30 minutes in about 850-degree-C peak. During baking of a resistor, a conductor ingredient is diffused [be / it / under / of a resistor / other side], and forms the interface field 14 which has an electrical property which is different in the bulk 16 of a resistor. The effect to TCR by which this interface field was measured is dependent on extent of diffusion of the conductor ingredient into a resistor, and the die length of a resistor. The effect to measured TCR becomes small, so that a resistor is long. TCR by which TCR with a high conductor runner was measured is raised above the bulk value of a resistor to the resistor of a low value. A silver conductor runner has the biggest effect to the measured TCR.

[0005]
[Problem(s) to be Solved by the Invention] As argued above, in using silver termination, there is antinomy nature of the engine performance with a short resistor. Such a resistor shows the serious problem brought about by diffusion of the silver from termination to the interior of a short resistor. It is the "die-length effectiveness" with serious one of the problem, and this depends for resistance (R) and the temperature coefficient of resistance (TCR) of a resistor on the die length of a resistor. The die-length effectiveness decreases by using Pd/Ag or golden termination, and can minimize a resistor / termination interaction. However, this approach is not desirable by the reason of clear cost.
[0006] Drawing 2 illustrates the die-length effectiveness of the thick film resistor which had termination made with silver. It is shown that the resistance decreases and TCR increases as the die length of a resistor decreases shorter than 2mm. It is : [0007] to which R and TCR of a resistor become independent of die length, and it will receive in design eye and R will follow the equation of a fundamental thick film if silver diffusion is prevented.
[Equation 1] R=Rsxn -- R is resistance, Rs is sheet resistance here, and n is l/w and is the number of square.
[0008] In addition to 1% of allowed value of + in resistance, or -, the resistor in a technical level is produced in TCR now by the allowed value of 100 ppm/degree C of + or -. In order to obtain a stricter allowed value in TCR, without increasing the magnitude and the price of a resistor, the new constituent for termination is required and it is made for the constituent to decrease the die-length effectiveness of the resistor terminated with silver. Therefore, this invention is RuO2 of the low resistance (less than 100ohms) terminated with silver. It is the approach of the low cost for decreasing the die-length effectiveness of a resistor, and the approach is because the negative driver and/or the metal hydride of TCR are added to a silver termination constituent.
[0009]
[Means for Solving the Problem] For this invention, said constituent is :a. on the basis of all constituents about a thick-film silver termination constituent. 60 - 80 % of the weight of silver dust objects;
b. Set to 400-650-degree C softening temperature and burning temperature, and it is 106. 0.1 - 15 % of the weight of particles of a glass binder which have the absolute viscosity of under a poise;
c. It is characterized by distributing a, b, and c in an organic vehicle here including 0.1 - 5 % of the weight of negative TCR drivers, and;.
[0010] This invention relates to the constituent by which the driver of negative TCR may be permuted by the hydride of the metal of four groups of the periodic table, and five groups further. A negative TCR driver may be similarly permuted by the fine particles (plurality) which may be combined with selection metal fine particles, a hydride, or a driver.
[0011]
[Embodiment of the Invention] In order to minimize the die-length effectiveness, as a conductor, it has lead borosilicate glass and a negative TCR driver as silver and an inorganic binder, and the termination constituent with abundant silver distributed by the organic screen-stencil vehicle is used. a TCR driver may be used separately, and may be combined, come out of and used. A TCR driver may be found out in glass, may be directly added to a silver termination constituent between grinding, or may be found out by those

both. The function of a TCR driver is to compensate the effectiveness of silver diffusion over R and TCR of a resistor. A TCR driver exists in 5 or less % of the weight of the amount of all the solid-states in termination.

[0012] As used here, TCR of a resistor is the measured value of resistance depending on temperature.

[0013] hot -- TCR (HTCR) -- and cold -- generally TCR (CTCR) is expressed by ppm/**, and is defined by (1) and (2).

[0014]

[Equation 2]

$$\text{HTCR in ppm/°C} = \frac{R_{125}-R_{25}}{R_{25}\,(125-25)} \times 10^6 \qquad (1)$$

$$\text{CTCR in ppm/°C} = \frac{R_{55}-R_{25}}{R_{25}\,(-55-25)} \times 10^6 \qquad (2)$$

[0015] Here, R25 is resistance expressed by omega/** in 25 degrees C (sq), R125 is resistance expressed with omega/** in 125 degrees C, and R-55 is resistance expressed with omega/** in -55 degrees C.

[0016] RuO2 by which adding a negative TCR driver (for example, oxide of Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb) was terminated with silver Although it is made to decrease the die-length effectiveness of a resistor The hydride (for example, TiH2, ZrH2, HfH2, CbH, ThH4, TaH) of the metal of four groups of a periodic table and five groups has found out the thing effective remarkably as a driver. These hydrides are decomposed, a reduction-ambient atmosphere is offered and it is surmised that generation of the complex ion (Ag+) which the reductant ambient atmosphere diffuses in resistor glass easily in very migratory is checked. The metal generated after decomposition has very high reactivity, and makes an alloy with abundant silver in termination. Since these metals are strong reducing agents, the oxidation to silver complex ion is checked further. A reactant metal oxidizes internally in silver after baking, and it is distributed over homogeneity, and it can use to the diffusion (what kind of complex ion to generate together) to resistor glass.

[0017] The TCR driver diffused on resistor glass makes R increase, and decreases TCR. Therefore, it compensates the effectiveness of diffusion of the complex ion to which decrease R and TCR is made to increase. By adjusting appropriately the class and concentration of a TCR driver in termination, the die-length effectiveness caused by diffusion of the complex ion to the inside of a resistor is essentially removable. the more detailed example of a TCR driver -- Sb 2O3, Fe 2O3, Fe 3O4, WO3, Nb 2O3, V2 O5, Cr 2O3, MoO3, TiO2, Mn 2O3, MnO3, Ta 2O5, and Co 2O3 it is .

[0018] Furthermore, it is very effective in metal fine particles like Ti, Nb, Mn, Fe, Co, Cr, W, Mo, V, and Sb being independent, or being added to silver termination in the combination accompanied by one, or the two above-mentioned hydrides or TCR drivers or more, and said metal fine particles minimizing the die-length effectiveness. The reduction-ambient atmosphere generated by decomposition of a hydride decelerates the oxidation rate of metal fine particles, and it is believed that metal fine particles were enabled to act as a reducing agent, and generation of complex ion is checked. After the oxidization which takes place as a result diffuses the oxide of metal fine particles into resistor glass, serves as a

negative TCR driver, and compensates R/TCR change caused by diffusion into the resistor of complex ion.

[0019] A silver dust object can have logy [like the shape of the shape of a piece, and a non-piece / various / MORUHO]. A non-flake powder object may be very good in an irregular form, and may be spherical. Preferably, the detailed shape of a piece and spherical silver dust object which has the average grain size of 1 micrometer is used.

[0020] Another component of the silver termination of this invention is low softening temperature glass, is 0.1 - 15% of the weight of the whole constituent, and is 0.1 - 10 % of the weight preferably, and is 0.1 - 2 % of the weight more preferably. Low softening temperature glass means the glass which has the softening temperature below 500 degrees C for the softening temperature below 650 degrees C preferably, and the softening temperature is measured by the fiber elongating method (ASTM C 338-57) of common use. Therefore, the glass binder in silver termination should have the softening temperature in the range of 400 degrees C - 650 degrees C. The function is giving promoting fusion and sintering of a silver granule child, and association to a substrate. The glass used for this invention also needs to have low viscosity in burning temperature. It sets to burning temperature and is 106. It is because the glass which has the absolute viscosity of under a poise satisfies the demand about this silver constituent and it promotes migration of the inorganic compound with which this glass was along the particle boundary and opening to the interior of a substrate body from a constituent.

[0021] The typical example of the glass with which are satisfied of the above conditions is Bi 2O3, and 40-60 at percentage by weight ;P They are bO, 28-37; and B-2 O3, and boric-acid bismuth lead glass containing 3-32. Especially desirable glass is Bi 2O3 and 60% ;P bO and 37%; and B-2 O3, and 3% are contained. in addition, aluminum 2O3, CaO, MgO, ZnO and TiO2, and ZrO2 etc. -- they are stable, endurance is high, and it offers having the softening temperature within the pointed-out limits, and the embellished lead borosilicate glass is also suitable. The example of other suitable low softening temperature glass :alumino lead borosilicate-zinc (Pb-Zn alumino-borosilicate), Lead borosilicate-zinc (Pb-Zn borosilicate) and HOUKEI acid zinc-copper (Zn-Cu borosilicate), HOUKEI acid alkali (alkali borosilicate), HOUKEI acid alkali-alumino (alkari-alumino borosilicate), hoe silicic-acid bismuth (Bi borosilicate), and hoe silicic-acid bismuth-zinc (Bi-Zn borosilicate) is included. When it calcinates in [containing a desirable burning temperature of 850 degrees C] 800-900 degrees C, a glass binder must give good conductivity, adhesion, and densification to silver termination.

[0022] Glass is formed of the glass manufacturing technology of common use, it is mixed by the ratio of a request of a desired component, or the precursor 3, for example, H3 BO to B-2 O3, and it is because the mixture is heated and melting liquid is formed. Processing between a certain time amount is performed to peak temperature, and the melting liquid becomes liquefied completely, and generating of gas ends heating as you may set on the technique concerned and it is known. In this activity, by swaying in a jar, the component carries out preliminary mixing, and then is dissolved in about 1000 degrees C in a platinum crucible. The melting liquid was poured out into cold water next, and after dissociating from strong cold water, the crude frit removed the water of survival by drying in oven. Next, alumina balls were used and the ball milling of the crude frit was underwater carried out over 40 hours. After taking out the frit slurry ground from the mill, the decantation removed

the superfluous solvent and frit fine particles were air-dried in the room temperature. The dry fine particles were sifted out through the screen of 60 meshes next, and any big particles were removed.

[0023] A glass powder object needs to have the grain size of less than 10 micrometers, and needs to have the grain size of less than 5 micrometers preferably. Similarly, in a diameter, a silver dust object and a TCR driver, or its precursor needs to have the grain size of less than 5 micrometers, and has about 1 micrometer preferably.

[0024] It distributes in an organic vehicle and the inorganic solid-state contents (silver, glass and inorganic materials, or those precursors) of the silver constituent of this invention form the constituent paste which can be printed. By mixing mechanically using a planet mold mixer, it is essentially mixed with an inactive liquid medium (vehicle), then a 3 roll kneading machine distributes, and an inorganic particle is the suitable workability (consistency) for screen-stencil. And the paste-like constituent which has a rheology was formed. The paste-like constituent of the latter is printed as a thick film on the ceramic substrate of common use in the approach of common use.

[0025] An inactive liquid may also be used for what kind of essential target as a vehicle. The various organic liquids which do not have or have a thickener, a stabilizing agent, and/or other common additives may be used as a vehicle. The example of a type of the organic solvent which can be used is the solution of the ethyl cellulose in a solvent like the solution (a thing like the polymethacrylate in lower alcohol) of the ester (it is (for example, like acetic ester and propionic-acid ester)) of fatty alcohol and said alcohol, a terpene (a thing like **, such as pine oil and a TERUPI nerol), and resin, pine oil, and ethylene glycol monoacetate butyl ether. A desirable vehicle uses as the base ethyl cellulose resin and alpha-, beta-, and gamma-TERUPI nerol (85 - 92% of alpha-TERUPI nerol which generally contains 8 - 15% of beta- and gamma-TERUPI nerol). A vehicle contains volatile fluid and may promote the high-speed coagulation after spreading to a substrate.

[0026] It depends for the ratio of the vehicle to the solid-state in a distributed object on an approach to change fairly and apply a distributed object and the class of vehicle. In order to realize good coating weight preferably, it is made for a distributed object to contain 60 - 90% of solid-state, and 40 - 10% of vehicle complementary as mentioned above. Of course, the constituent of this invention may be embellished by adding other ingredients which do not affect the useful property. Such a formula is known well for this contractor.

[0027] A paste is idiomatically adjusted by the 3 roll kneading machine. When it measures with the Brookfield (Brookfield) HBT viscometer in low, inside, and a high shear rate, the viscosity of a paste is the following within the limits typically.

[0028]

[Table 1]

剪断速度(sec^{-1})	粘度 (Pa·s)	
0.2	100-5000	
	300-2000	好ましい
	600-1500	最も好ましい
4	40-400	
	100-250	好ましい
	140-200	最も好ましい
40	10-150	
	25-120	好ましい
	50-100	最も好ましい

[0029] The amount of a vehicle is determined by the viscosity of a formula of a final request.

[0030] The silver constituent of this invention can be printed as a film on a substrate by using either an automatic printer or a manual printer by the approach of common use. Preferably, an automatic screen stencil-printing technique is used using the screen of 200 meshes.

[0031] The capacity to decrease the die-length effectiveness of the low ohm thick film resistor of the silver termination containing a negative TCR driver or metal hydride on parenchyma, or to remove it is RuO2 as a main electric conduction phase. It is limited to the resistor to contain. A low ohmic resistance object lower than 100ohms / ** is Pd/Ag of more amounts than 10 % of the weight as current operation is carried out in industry RuO2 It realizes by combining and adding as an electric conduction phase. Such a resistor shows the die-length effectiveness which is not sensitive to addition of the negative TCR driver to the inside of termination.

[0032] Generally the high ohmic resistance object which similarly has the sheet resistance exceeding 100ohms / ** is replaced with what is used for a low ohmic resistance object, and the glass which has higher viscosity and softening temperature is used. Such resistor glass tends to make late the diffusion rate of the complex ion from termination to into a resistor, and causes the die-length effectiveness smaller than that by which the inclination was observed in the low ohmic resistance object.

[0033] therefore, the main applications of this invention -- a low ohmic resistance object -- setting -- coming out -- it is -- the glass of the low softening temperature [resistor / this] in hypoviscosity -- using -- a lot of RuO2 It is required to distribute an electric conduction phase and to obtain low resistance value. Although the new termination of this invention may be used with a high ohmic resistance object, an improvement of the observed die-length effectiveness is not big. Because, it is because diffusion of the negative TCR driver (and complex ion) which lets hyperviscous glass pass in the burning temperature of 850 degrees C is decreasing on parenchyma.

[0034] In preparation of the constituent of a formula and spreading this invention, a granular inorganic solid-state is mixed with an organic medium, and a constituent with which it distributes using a suitable device like a 3 roll kneading machine, suspension is formed, and viscosity becomes an about 100-200 pascal-second in the shear rate of 4sec-1 is given.

[0035] In the continuing example, the formula was performed by the following approaches.

[0036] Weighing capacity of the component of a paste is carried out together in a container. The component passes a disperser like a 3 roll kneading machine for; which is mixed violently next and forms the compound of homogeneity, next its compound, and realizes good distribution of a particle. In order to determine the condition of distribution of the particle under paste, the Hegemann gage (Hegman gauge) was used. It inclines so that this measuring instrument may consist of slots under metal block, and that slot may have a depth of 25 micrometers (1mil) at one end and it may become the depth 0 at another end. A blade is used. A paste is pulled down along the die-length direction of the slot. It is a scratch (scratch) to a slot in a larger place than the depth of the diameter fang furrow of an aggregate. It appears. Enough distributed objects come to give the 10-18-micrometer scratch point of 1/4 typically. The point that one half of slots was exposed using the paste distributed good is 3-8 micrometers typically. > 1/4 20-micrometer measurement and 1/2 measurement of >10micrometer point out the suspension distributed imperfectly.
[0037] Next, on a substrate like alumina ceramics, generally, a constituent reaches and is most preferably applied to the humid thickness of 40-50 microns by 35-70 microns of about 30-80 microns of processes of screen-stencil. The constituent of this invention can be applied on a substrate using either an automatic printer or a manual printer by the approach of common use, and the automatic screen-stencil technique using the screen of the 325-mesh from 200- is used preferably. The printed pattern is about 150 degrees C under from 200 degrees C next, and is dried over about 5 - 15 minutes before baking. The band-conveyor furnace at which baking for sintering both inorganic binder and particle of the metal divided minutely was ventilated effectively preferably is used. The band-conveyor furnace damages an organic substance by fire in about 300 degrees C - 600 degrees C, and the cooling process by which the period of an about 800 degrees C - 1000 degrees C maximum temperature continued for abbreviation 5 to 15 minutes, and was controlled following it prevents fracture of the substrate which superfluous sintering, the unnecessary chemical reaction in an intermediate temperature, or too quick cooling causes following it. All baking procedures are preferably continued exceeding the period for about 30 - 60 minutes. In 10 - 25 minutes, the baking procedure reaches the burning temperature of 850 degrees C, and is said to about 10 minutes and cooling as about 10 - 25 minutes in burning temperature. In some cases, complete-cycle time amount may be short used like 7 - 14 minutes of 20 - 30 minutes by baking of common use, and infrared baking.
[0038] By introducing an actual example indicates this invention covering the further detail. However, the range of this invention is not limited by these actual examples in any semantics.
[0039] All the values given to front Naka are the percentage by weight to all constituents.
[0040]
[Example] The following constituents are available silver termination constituents commercially, and are enumerated how.
[0041]
Constituent A - Silver termination constituent 5426 constituent B - Silver termination constituent QS171 constituent C - Silver termination constituent 6160 constituents A, B, and C are more nearly available than I eye E. I. du Pont de Nemours dough NUMURU- and - company (E.I.Du Pont de Nemours and Company, Wilmington, DE).
[0042] Similarly, a thing as shown in Table 2 is the silver termination constituent of the

addition which may be used for this invention.

[0043]

[Table 2]

	D	E	F	G	H	I
Ag	73.35	72.40	72.40	72.40	72.40	72.40
Pd	0.55	0.60	0.60	0.60	0.60	0.60
Bi_2O_3						
PbO_2						
Cu_2O						
Cr						1.00
*W			1.00			
* Wsi_2				1.00		
* TiH_2	1.55	1.04	0.69	0.69	0.9	0.69
(エチルセルロース/テルピネオール) 有機ビヒクル	23	24.8	24.5	24.5	25.1	24.5
フリットI		0.67	0.45	0.45	0.59	0.45
フリットII	0.31					
フリットIII	0.93					
フリットIV		0.09	0.06	0.06	0.78	0.06
フリットV		0.23	0.15	0.15	0.2	0.15
フリットVI	0.31	0.22	0.15	0.15	0.2	0.15

*TCRドライバー

[0044] The frit constituent used in constituent D-I is found out by Table 3.

[0045]

[Table 3]

ガラス組成物全体を基準とする重量パーセント						
	I	II	III	IV	V	VI
酸化物						
PbO	55.9	66	51	78.1		
SiO_2	28	23	26.1		24.9	
B_2O_3	8.1	8.5	6.94		6.46	
Al_2O_3	4.7	2.5	6.69			
*TiO_2	3.3		4.56		13.8	
ZnO			2.79			
CuO						9.1
*MnO					54.8	
CaO						
GeO_2				21.9		90.9
Bi_2O_3						
	100	100	100	100	100	100

*TCRドライバー

[0046] It sets by examples 1-67, and silver termination is printed on the resistor (R1-R4) of 10 ohms of nominal ratings. This resistor is used and the general usefulness of this invention in decreasing remarkably the die-length effectiveness generally observed in the short resistor terminated using silver is explained. the electric conduction phase of those resistors -- RuO2 it is -- in order to acquire the sheet resistance of low 10ohms / ** -- typical -- RuO2 of 40% of the weight or more of a solid amount It exists. Although the glass properties of those resistors differ remarkably, those resistor glass is the low softening

temperature of the range of 400-650 degrees C and good humidity, distribution, and RuO2. It has the low viscosity in the range of 800-900-degree C burning temperature which makes possible densification by sintering of an electric conduction phase. The resistor constituents R2 and R3 are commercial constituents, and are identified as follows.

[0047]

R2 - Resistor constituent 2011R3 - A resistor constituent is the mixture of the weight ratios 50/50 of 2011 and 1711.

[0048] Constituents R2 and R3 are more nearly available than I eye E. I. du Pont de Nemours dough NUMURU- and - company (E.I.Du Pont de Nemours and Company, Wilmington, DE).

[0049] The constituent of R1 and R4 is given to Table 4.

[0050]

[Table 4]

成分	R1一重量%	成分	R4一重量%
RuO_2	41.04	RuO_2	40.32
Ag_2O	1.44	Ag_2O	1.44
MnO_2	0.36	TiO_2	1.44
a	2.16	a	2.16
b	2.88	d	14.40
c	4.68	e	8.64
d	19.44	f	3.60
*有機ビヒクル	28.00	*有機ビヒクル	28.00

*有機ビヒクルーエチルセルロースおよびテルピネオール

[0051] The formula of a-f is given to Table 5.

[0052]

[Table 5]

	a	a_1	b	c	d	e	f
Al_2O_3		1.1					
BaO							20.90
BiO_2		75.1					
B_2O_3			18.24	6.80	8.5	3.08	28.02
CuO	14.0					2.76	
CaO		2.4					5.96
MgO							5.50
MnO				9.41			
MnO_2	21.5						
Nb_2O_5			16.32				
P_2O_5							1.86
PbO		10.9	6.33	52.80	66.0	58.90	
SiO_2		9.3	3.84	18.40	23.0	29.52	11.19
TiO_2				10.59			
ZnO	14.5	1.2	55.28			2.59	9.34
ZrO_2							6.62
a_1	50.0						

[0053]

[Table 6]

				順次焼成された終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
1	R1	A	None	280	52	219	-18	228	237
2	R1	A+	1.5% TiO_2	110	115	86	90	-5	-4
3	R1	A+	3.0% TiO_2	-194	-73	-302	-160	-121	-142
4	R1	A+	4.0% Nb_2O_5	124	21	55	-52	103	107
5	R1	A+	4.0% MnO_2	138	32	57	-41	106	98
6	R1	B	None	470	72	439	5	398	434
7	R1	B+	1.5% TiO_2	111	113	79	75	-2	4
8	R1	B+	3.0% TiO_2	-146	-58	-248	-143	-88	-105
9	R1	B+	4.0% Nb_2O_5	336	53	290	-16	283	306
10	R1	B+	4.0% MnO_2	300	56	243	-14	244	257
11	R1	C	None	259	47	204	-24	212	228
12	R1	C+	1.5% TiO_2	-100	-138	-162	-202	38	40
13	R1	C+	3.0% TiO_2	-474	-247	-634	-367	-227	-267
14	R1	C+	4.0% Nb_2O_5	95	23	22	-51	72	73
15	R1	C+	4.0% MnO_2	137	26	58	-49	111	107

[0054]
[Table 7]

				共焼成した終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
1	R1	A	None	258	47	193	-23	211	216
2	R1	A+	1.5% TiO_2	-6	-1	-91	-77	-5	-14
3	R1	A+	3.0% TiO_2	-237	-87	-350	-177	-150	-173
4	R1	A+	4.0% Nb_2O_5	90	14	18	-59	76	77
5	R1	A+	4.0% MnO_2	100	27	13	-49	73	62
6	R1	B	None	550	79	522	13	471	509
7	R1	B+	1.5% TiO_2	174	35	112	-36	139	148
8	R1	B+	3.0% TiO_2	-175	-57	-278	-141	-118	-137
9	R1	B+	4.0% Nb_2O_5	356	58	309	-11	298	320
10	R1	B+	4.0% MnO_2	329	53	272	-18	276	290
11	R1	C	None	273	47	217	-24	226	241
12	R1	C+	1.5% TiO_2	-50	-15	-140	-93	-35	-47
13	R1	C+	3.0% TiO_2	-422	-196	-570	-308	-226	-262
14	R1	C+	4.0% Nb_2O_5	61	5	-15	-70	56	55
15	R1	C+	4.0% MnO_2	146	25	67	-49	121	116

[0055]
[Table 8]

				順次焼成された終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
16	R2	A	None	158	17	84	-72	141	156
17	R2	A+	1.5% TiO_2	-47	-45	-117	-116	-2	-1
18	R2	A+	3.0% TiO_2	-259	-60	-222	-158	-199	-64
19	R2	A+	4.0% Nb_2O_5	-121	-46	-234	-142	-75	-92
20	R2	A+	4.0% MnO_2	153	13	70	-75	140	145
21	R2	B	None	337	39	274	-46	298	-235
22	R2	B+	1.5% TiO_2	200	204	169	173	-4	35
23	R2	B+	3.0% TiO_2	-19	-31	-116	-124	12	85
24	R2	B+	4.0% Nb_2O_5	66	-2	-23	-91	68	21
25	R2	B+	4.0% MnO_2	287	31	218	-55	256	-187
26	R2	C	None	173	18	94	-69	155	163
27	R2	C+	1.5% TiO_2	69	7	36	-34	62	70
28	R2	C+	3.0% TiO_2	-171	-74	-301	-181	-97	-120
29	R2	C+	4.0% Nb_2O_5	-99	-37	-210	-133	-62	-77
30	R2	C+	4.0% MnO_2	171	17	90	-71	154	161

[0056]
[Table 9]

				共焼成した終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
16	R2	A	None	138	17	52	-72	121	124
17	R2	A+	1.5% TiO_2	-42	-29	-145	-124	-13	-21
18	R2	A+	3.0% TiO_2	-151	-67	-271	-166	-84	-105
19	R2	A+	4.0% Nb_2O_5	-112	-51	-231	-148	-61	-83
20	R2	A+	4.0% MnO_2	151	14	65	-75	137	140
21	R2	B	None	427	20	370	-40	407	410
22	R2	B+	1.5% TiO_2	180	-17	106	-69	197	175
23	R2	B+	3.0% TiO_2	-1	6	-99	-107	-7	8
24	R2	B+	4.0% Nb_2O_5	120	31	31	-82	89	113
25	R2	B+	4.0% MnO_2	319	19	250	-56	300	306
26	R2	C	None	196	19	122	-68	177	190
27	R2	C+	1.5% TiO_2	-54	-20	-152	-113	-34	-39
28	R2	C+	3.0% TiO_2	-14	-65	-257	-165	51	-92
29	R2	C+	4.0% Nb_2O_5	-96	-45	-206	-142	-51	-64
30	R2	C+	4.0% MnO_2	185	17	103	-73	168	176

[0057]
[Table 10]

				順次焼成された終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
31	R3	A	None	98	-32	11	-122	130	133
32	R3	A+	3.0% TiO_2	-270	-199	-408	-320	-71	-88
33	R3	A+	4.0% Nb_2O_5	-152	-88	-276	-187	-64	-89
34	R3	A+	4.0% MnO_2	67	-37	-27	-128	104	101
35	R3	B	None	226	-5	148	-91	231	239
36	R3	B+	3.0% TiO_2	-60	-77	-175	-174	17	-1
37	R3	B+	4.0% Nb_2O_5	6	-48	-93	-141	54	48
38	R3	B+	4.0% MnO_2	193	-18	115	-106	211	221
39	R3	C	None	108	-23	28	-110	131	138
40	R3	C+	3.0% TiO_2	-449	-334	-616	-478	-115	-138
41	R3	C+	4.0% Nb_2O_5	-264	-107	-389	-209	-147	-180
42	R3	C+	4.0% MnO_2	90	-27	-2	-116	117	114

[0058]
[Table 11]

				共焼成した終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
31	R3	A	None	127	-24	54	-112	151	166
32	R3	A+	3.0% TiO_2	-294	-165	-442	-280	-129	-162
33	R3	A+	4.0% Nb_2O_5	-154	-80	-281	-178	-74	-103
34	R3	A+	4.0% MnO_2	98	-28	8	-118	126	126
35	R3	B	None	281	1	214	-83	280	297
36	R3	B+	3.0% TiO_2	-113	-101	-233	-203	-12	-30
37	R3	B+	4.0% Nb_2O_5	60	-36	-29	-126	96	97
38	R3	B+	4.0% MnO_2	226	-11	154	-98	237	252
39	R3	C	None	135	-12	65	-98	147	163
40	R3	C+	3.0% TiO_2	-431	-270	-594	-402	-161	-192
41	R3	C+	4.0% Nb_2O_5	-257	-110	-396	-213	-147	-183
42	R3	C+	4.0% MnO_2	99	-21	8	-108	120	116

[0059]
[Table 12]

				順次焼成された終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
43	R1	A	None	280	52	219	-18	228	237
44	R1	A+	3%NbH	141	22	69	-52	119	121
45	R2	A	None	158	17	84	-72	141	156
46	R2	A+	3%NbH	-27	-44	-132	-141	17	9
47	R3	A	None	98	-32	11	-122	130	133
48	R3	A+	3%NbH	32	-57	-52	-154	89	102
49	R1	C	None	259	47	204	-24	212	228
50	R1	C+	3%NbH	50	15	-30	-62	35	32
51	R2	C	None	173	18	94	-69	155	163
52	R2	C+	3%NbH	-101	-35	-211	-131	-66	-80
53	R3	C	None	108	-23	28	-110	131	138
54	R3	C+	3%NbH	-232	-111	-366	-216	-121	-150
55	R2	A	None	158	17	84	-72	141	156
56	R2	A+	1% TiH_2	110	19	28	-68	91	96
57	R2	A+	3% TiH_2	-99	-18	-205	-108	-81	-97

[0060]
[Table 13]

				共焼成した終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
43	R1	A	None	258	47	193	-23	211	216
44	R1	A+	3%NbH	132	28	57	-46	104	103
45	R2	A	None	138	17	52	-72	121	124
46	R2	A+	3%NbH	77	-5	-16	-98	82	82
47	R3	A	None	127	-24	54	-112	151	166
48	R3	A+	3%NbH	18	-54	-75	-151	72	76
49	R1	C	None	273	47	217	-24	226	241
50	R1	C+	3%NbH	57	10	-25	-67	47	42
51	R2	C	None	196	19	122	-68	177	190
52	R2	C+	3%NbH	-94	-95	-192	-176	1	-16
53	R3	C	None	135	-12	65	-98	147	163
54	R3	C+	3%NbH	-246	-128	-369	-235	-118	-134

[0061]
[Table 14]

				順次焼成された終端／抵抗体				dHTCR	dCTCR
例番号	抵抗体番号	終端組成物	添加物重量%	HTCR 0.25mm	HTCR 1.25mm	CTCR 0.25mm	CTCR 1.25mm	(0.25-1.25mm)	
58	R2	A+	3% Nb_2O_5	50	9	-36	-78	41	42
59	R2	A+	3% $MnTiO_3$	41	8	-51	-80	33	29
60	R2	A+	3% TiC	102	14	15	-73	88	88
61	R2	A+	3% Ag_2WO_4	59	0	-27	-88	59	61
62	R4	A	None	273	109	260	88	164	172
63	R4	A+	3% Nb_2O_5	218	105	200	84	113	116
64	R4	A+	3% $MnTiO_3$	74	78	25	50	-4	-25
65	R4	A+	3% TiC	215	102	194	81	113	113
66	R4	A+	3% Ag_2W0_4	121	76	98	53	45	45
67	R4	A+	3% TiH_2	129	81	104	57	48	47

[0062] It is convenient to use the difference (dHTCR and dCTCR) in TCR of a between with a die length [of 0.25mm] and a die length of 1.25mm as criteria of the die-length effectiveness to the comparative purpose, referring to Table 14 from Table 6. dHTCR and a dCTCR value are found out by the train by which the label was carried out such in Table 11 from Table 6 about the termination/resistor co-burned about the termination / resistor by which sequential baking was carried out.

[0063] As shown in Table 6 to the table 11, they are TiO2 and Nb 2O5. And MnO2 When a driver is added by Termination A, B, and C, TCR of a resistor is ** made into a negative direction to the termination which is not doped. Data are given about the case by which sequential baking of die length of 0.25mm and the 1.25mm resistor was carried out with termination in the profile for 850 degrees C / 30 minutes of a criterion where it reached and co-burns. TCR of the resistor terminated using the termination A, B, and C which does not contain an additive is also shown for the comparison purpose.

[0064] In each ****, TCR is ** made more into the negative direction with the driver additive [as opposed to termination in forward TCR with short high 0.25mm resistor]. Therefore, it is possible by controlling the concentration of the TCR driver to termination to adjust TCR of a resistor to + / -100 ppm [degree C] /or a better allowed value. the line by which the label was carried out to dHTCR and dCTCR was doped by the driver -- it is -- it is -- the difference of the TCR value between resistors (0.25mm after [by which sequential baking was carried out in the termination which is not doped] reaching and co-burning, and 1.25mm) is given. The die-length effectiveness of the resistor generally given as dHTCR and dCTCR into Table 6 to the table 14 is decreasing considerably, when the termination by which the driver was doped is used.

[0065] TiO [on biasing toward a negative direction TCR of a resistor short in order to compensate forward TCR which diffusion of the complex ion to the inside of a resistor causes, and as opposed to termination]2 Addition is Nb 2O5 at weight criteria. And MnO2 It is effective. An example is 1% of TiO2 added to silver termination. Having changed TCR of 0.25mm resistor exceeding -100ppm/degree C is shown.

[0066] the TCR driver additive to the termination to which the data of Table 12 to the table 14 decrease in number the die-length effectiveness -- for example, TiO2 and Nb 2O5 And MnOX etc. -- it is shown that there is no need of being limited to a simple oxide. The compound of Ti, Nb, W, and Mn is also equally effective. MnTiO [as opposed to / as shown in Table 7 / Termination A]3, TiC, Ag2 WO4, and NbH and TiH2 The die-length effectiveness in which addition decreased as compared with the termination A which is not doped was produced as a result. Slight TiH2 to termination The remarkably effective thing was found out in addition decreasing the die-length effectiveness of a resistor. TiH2 It decomposes to Ti metal during baking, and the metal alloys with silver termination The generated hydrogen gives a reduction-ambient atmosphere and it is believed that it can promote that the ambient atmosphere prevents formation of complex ion and diffusion into a resistor. This device that became together with contribution of the powerful TCR driver from TiO2 is very effective in minimizing the die length effectiveness in a resistor.

[0067] W and WoI2 when referring to drawing 3 And TiH2 of metal reducing agents such as Cr, RuO2 also with the short addition (silver termination constituents F, G, and I found out all over Table 2) to the combined silver termination It found out that it was effective in setting and controlling the die-length effectiveness. A metal reducing agent is TiH2 of a complement in order to improve the die length effectiveness. As it makes it possible to return and is shown in the curves F, G, and I in drawing 3 , delicate adjustment of the property of the die length effectiveness is enabled.

[0068] Drawing 3 is shown as a function of the die length of the 10ohm resistor R1 of nominal ratings which carried out sequential baking of the HTCR on termination with various abundant silver. HTCR of R1 accompanied by Constituent A increases according to resistor die length decreasing, and this is a property observed typically However, the curve to Constituents E, F, G, and I (found out by Table 2) is the type of this invention, and these curves show reduction or that the die length effectiveness can quite be eliminated mostly by suitable addition to silver termination.

[0069] It sets to bias TCR of R2 toward a negative direction, and is MnO2 Addition should be cautious of it having not been effective. Because, this 10 ohm resistor contained MnO of a significant amount, is already saturated, therefore is MnO2 of the addition from termination. It had almost no effectiveness to the die length effectiveness of a resistor.

[0070] Drawing 4 illustration an improvement of the die length effectiveness which can be acquired by operation of this invention This drawing is the die-length effectiveness of 10 ohm resistor terminated using standard silver termination (termination A) TiH2 of this invention It is comparing with the die length effectiveness acquired using the doped silver termination.

[0071]

[Effect of the invention] It is made for the constituent to decrease the die length effectiveness of the resistor terminated with silver about the new constituent for the termination for obtaining a stricter allowed value in TCR, without the effectiveness of this invention increasing the magnitude and the price of a resistor. RuO2 of the low resistance (less than 100ohms) by which this invention was terminated with silver the approach of the low cost for decreasing the die-length effectiveness of a resistor -- it is -- the driver and/or metal hydride of TCR negative in the approach -- and/or, metal fine particles are depended on adding to a silver termination constituent.